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16. ABSTRACT

The Analytical Quality Control Laboratory of the U.S. Environmental Protection Agency (EPA), conducted a preliminary interlaboratory study on analysis of organic and inorganic mercury by the cold vapor technique.
Sample concentrates were prepared at four mercury levels and furnished to the analysts with the known values. Analysts added an aliquot of each concentrate to distilled water and to a surface water of their choice. Single analyses were made on the distilled and on the surface water samples with and without the known increments, using the EPA Method and a method of their choice (Other Method). Recoveries were compared. The accuracy and precision of the methods were noted as were interferences from natural water samples.
In this comparative study, the EPA Method was equal or superior to the Other Method in accuracy and precision in 80% of tests. More significantly, in those samples containing organic mercury, the EPA Method was equal or superior to the Other Method. This study indicates that if water samples contain mercury in organic form, a method involving a vigorous digestion step such as that in the EPA Method must be used to obtain a good recovery.

17. KEY WORDS AND DOCUMENT ANALYSIS

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# Analyses for Mercury in Water

## A PRELIMINARY STUDY OF METHODS

National Environmental Research Center
Office of Research and Monitoring
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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# ANALYSES FOR MERCURY IN WATER
## A PRELIMINARY STUDY OF METHODS

John A. Winter and Harold A. Clements
Method and Performance Evaluation Activity
The Analytical Quality Control Laboratory
1014 Broadway, Cincinnati, Ohio 45202

Program Element 1H1327

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

# FOREWORD

To find, through research, the means to protect, preserve, and improve our environment, we need a focus that accents the interplay among the components of our physical environment -- the air, water, and land. The missions of the National Environmental Research Centers -- in Cincinnati, Research Triangle Park, N.C., Corvallis, Oregon, and Las Vegas, Nevada -- provide this focus. The research and monitoring activities at these centers reflect multidisciplinary approaches to environmental problems; they provide for the study of the effects of environmental contamination on man and the ecological cycle and the search for systems that prevent contamination and recover valuable resources.

Man and his supporting envelope of air, water, and land must be protected from the multiple adverse effects of pesticides, radiation, noise, and other forms of pollution as well as poor management of solid waste. These separate pollution problems can receive interrelated solutions through the framework of our research programs -- programs directed to one goal -- a clean livable environment.

This publication of the National Environmental Research Center, Cincinnati, entitled: *Analyses for Mercury in Water, A Preliminary Method Study* reports the results of a broad study of methods currently in use in the United States and Canada for analysis of mercury in waters. Federal agencies, states, municipalities, universities, private laboratories, and industry should find this comparative study of methods of analysis for mercury of vital importance in their efforts at monitoring and controlling mercury pollution in the environment.

ANDREW W. BREIDENBACH, Ph.D.
Director, National Environmental
Research Center, Cincinnati

# PREFACE

The Office of Research and Monitoring, EPA, coordinates the collection of water quality data to determine compliance with water quality standards, to provide information for planning of water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research activities. In a large measure, the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

The Analytical Quality Control Laboratory, NERC, Cincinnati, is responsible for insuring the reliability of physical, chemical, biological, and microbiological data generated in the water programs of EPA. Within the Analytical Quality Control Laboratory, the Method and Performance Evaluation (M&PE) Activity conducts the inter-laboratory studies of analytical procedures to:

1) assist in the selection of EPA methods,
2) evaluate the selected methods of analyses, and
3) measure the performance of EPA analysts and laboratories.

This report describes one study in the series conducted by the M&PE Activity.

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Staff of the
Method and Performance Evaluation Activity, Analytical Quality Control Laboratory

John A. Winter, Chief
Harold A. Clements, Senior Chemist
Guy F. Simes, Chemist
Everett L. Barnett, Chemist
Betty J. Smith, Secretary



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## PARTICIPATING LABORATORIES

Forty-two analysts in 42 laboratories reported results of the analyses of the mercury reference samples. Of the 42 laboratories, 32 were non-EPA laboratories. The participating laboratories were:

### U.S. Environmental Protection Agency Laboratories

Advanced Waste Treatment Research Laboratory
National Environmental Research Center
Cincinnati, Ohio

Analytical Quality Control Laboratory
Trace Metals Analyses Group
National Environmental Research Center
Cincinnati, Ohio

National Field Investigations Center
Office of Enforcement & General Counsel
Cincinnati, Ohio

Edison Water Quality Research Laboratory
National Environmental Research Center
Edison, New Jersey

Indiana District Office
Region V
Evansville, Indiana

National Water Quality Laboratory
Duluth, Minnesota

Pacific Northwest Environmental Research Laboratory
National Environmental Research Center
Corvallis, Oregon

Southeast Environmental Research Laboratory
National Environmental Research Center
Athens, Georgia

Surveillance & Analysis Division
Technical Support Branch
Region IX
Alameda, California

Wheeling Field Station
Region III
Wheeling, West Virginia

## Non-EPA Laboratories

Bohna Engineering & Research, Inc.
San Francisco, California

Deer Island Treatment Plant
Winthrop, Massachusetts

Diamond Shamrock Chemical Company
Painesville, Ohio

Diamond Shamrock Chemical Company
Sheffield, Alabama

Division of Water Resources
Charleston, West Virginia

E. I. du Pont de Nemours & Co. (Inc.)
Savannah River Laboratory
Aiken, South Carolina

E. I. du Pont de Nemours & Co. (Inc.)
Savannah River Plant, Lab. Division
Aiken, South Carolina

Georgia Kraft Research Company
Rome, Georgia

Georgia-Pacific Corporation
Bellingham Division
Bellingham, Washington

Georgia Water Quality Control Board
Atlanta, Georgia

Instrumentation Laboratory, Inc.
Lexington, Massachusetts

International Paper Company
Mobile, Alabama

Massachusetts Division of Fish & Game
Westborough, Massachusetts

Milwaukee Department of Public Works
Milwaukee, Wisconsin

Monsanto Corporation
Sauget, Illinois

National Council of Paper Industry
for Air & Stream Pollution
Gainesville, Florida

Water Quality Control Laboratory
Stanford University
Stanford, California

New Hampshire Water Supply & Pollution
Control Commission
Pesticide Surveillance Laboratory
Concord, New Hampshire

North Carolina Department of Water
& Air Resources
Raleigh, North Carolina

North Carolina State Board of Health
Laboratory Division
Raleigh, North Carolina

Oregon State Department of Environmental
Quality
Portland, Oregon

South Carolina Pollution Control
Authority
Columbia, South Carolina

T. W. Beak Consultants Limited
Toronto, Canada

Texas A & M University
Agriculture Analytical Service
College Station, Texas

Toms River Chemical Corporation
Toms River, New Jersey

U. S. Geological Survey
Denver, Colorado

U. S. Geological Survey
Ocala, Florida

Union Oil Company
Los Angeles Refinery
Wilmington, California

University of Illinois
College of Agriculture
Urbana, Illinois

University of Missouri
Environmental Trace Substances Center
Columbia, Missouri

Water Pollution Research Laboratory
Stevenage, England

Westvaco Research Center
Laurel, Maryland

ANALYSES FOR MERCURY IN WATER, A PRELIMINARY METHOD STUDY

## SUMMARY

The Analytical Quality Control Laboratory, National Environmental Research Center--Cincinnati, of the U.S. Environmental Protection Agency (EPA), conducted a preliminary interlaboratory study on analysis of organic and inorganic mercury by the cold vapor technique.

Sample concentrates were prepared at four mercury levels and furnished to the analysts with the known values. Analysts added an aliquot of each concentrate to distilled water and to a surface water of their choice. Single analyses were made on the distilled and on the surface water samples with and without the known increments, using the EPA Method and another of their choice (Other Method). Recoveries were compared. The accuracy and precision of the methods were noted as were interferences from natural water samples.

In this comparative study of the EPA Method and Other Method, the EPA Method was equal or superior to the Other Method in accuracy and precision in 80% of all tests. More significantly, in those samples containing organic mercury with or without inorganic mercury, the EPA Method was equal or superior to the Other Method. This study indicates that if water samples contain mercury in organic form, a method involving a vigorous digestion step such as that in the EPA Method must be used to obtain a good recovery. On pages *xiv* and *xv* a statistical summary of this data shows the precision and accuracy measurements obtained in this study.



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## Statistical Summary

Recovery of Inorganic Mercury ($HgCl_2$) from Distilled Waters

| | Sample 1 | | Sample 2 | |
|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method |
| True Value, µg/liter | 0.34 | 0.34 | 4.2 | 4.2 |
| Mean Recovery, µg/liter | 0.341 | 0.409 | 3.94 | 3.86 |
| Accuracy as % Relative Error (Bias) | 0.3 | 20.2 | -6.3 | -8.0 |
| Standard Deviation, µg/liter | 0.07 | 0.16 | 0.54 | 0.77 |
| Relative Deviation, % | 19.5 | 40.0 | 13.6 | 19.9 |
| Range, µg/liter | 0.32 | 0.80 | 2.5 | 3.6 |

Recovery of Inorganic Mercury ($HgCl_2$) from Natural Waters

| | Sample 1 | | Sample 2 | |
|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method |
| True Value, µg/liter | 0.34 | 0.34 | 4.2 | 4.2 |
| Mean Recovery, µg/liter (By Difference) | 0.351 | 0.369 | 3.99 | 4.34 |
| Accuracy as % Relative Error (Bias) | 3.2 | 8.5 | -5.1 | 3.3 |
| Standard Deviation, µg/liter | 0.07 | 0.12 | 0.66 | 0.60 |
| Relative Deviation, % | 19.8 | 31.5 | 16.6 | 13.8 |
| Range, µg/liter | 0.25 | 0.40 | 3.3 | 2.2 |

## Statistical Summary

Recovery of Organic and Inorganic Mercury (Phenyl Mercuric Acetate-$HgCl_2$) from Distilled Waters

| | Sample 3 Organic & Inorganic Mercury | | Sample 4 Organic Mercury Alone | |
|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method |
| True Value, µg/liter | 6.3 | 6.3 | 4.2 | 4.2 |
| Mean Recovery, µg/liter | 6.10 | 5.23 | 4.02 | 3.02 |
| Accuracy as % Relative Error | -3.1 | -17.0 | -4.2 | -28.0 |
| Standard Deviation, µg/liter | 0.68 | 1.45 | 0.80 | 1.53 |
| Relative Deviation, % | 11.2 | 27.8 | 19.8 | 50.7 |
| Range, µg/liter | 4.0 | 7.0 | 4.5 | 4.8 |

Recovery of Organic and Inorganic Mercury (Phenyl Mercuric Acetate-$HgCl_2$) from Natural Waters

| | Sample 3 Organic & Inorganic Mercury | | Sample 4 Organic Mercury Alone | |
|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method |
| True Value, µg/liter | 6.3 | 6.3 | 4.2 | 4.2 |
| Mean Recovery, µg/liter (By Difference) | 5.61 | 6.15 | 3.83 | 3.30 |
| Accuracy as % Relative Error | -10.9 | -2.4 | -8.7 | -21.4 |
| Standard Deviation, µg/liter | 1.27 | 1.06 | 1.07 | 1.48 |
| Relative Deviation, % | 22.7 | 17.2 | 27.9 | 45.0 |
| Range, µg/liter | 5.3 | 3.8 | 5.3 | 4.1 |

# INTRODUCTION

This preliminary study on methods of analysis for mercury in water was conducted to develop further information on the ability of the analytical methods to measure total mercury, i.e., organic plus inorganic mercury.

It differs from formal method studies in that the analysts received the true value data with the samples. The main purpose of the study was to make a preliminary comparison of methods for mercury analysis performed with known concentrations of organic and inorganic mercury added to distilled and natural water samples. Analysts used different digestion reagents, different volumes of reagents and varied the times and temperatures and separation techniques. The mercury concentration was detected and measured by cold vapor technique using an atomic absorption spectrophotometer, Coleman mercury meter or UV/visible spectrophotometer. One laboratory used an emission spectrographic procedure.

It should be pointed out that the Other Method(s) used in this study are really the methods of choice of the laboratories participating in the study. As these methods are those in routine use, familiarity and confidence in the procedures would tend to favor the Other Method over the proposed EPA procedure in some laboratories.

## DESCRIPTION OF STUDY

### Sample Design

In this comparison of methods for mercury analyses, the test design was as follows:

1. Each sample was prepared as a stable concentrate in a sealed glass ampul.
2. When an aliquot of the concentrate was diluted to volume, the mercury was present at levels found in waters and wastewater. Several levels of concentration were tested to cover the range of levels found in surface waters and wastewater.
3. The sample concentrates containing known increments of organic and/or inorganic forms of mercury were added to distilled water and to a surface water of choice and the samples analyzed. The surface waters were analyzed with and without increments and the added level determined by difference.
4. Recoveries in distilled and surface waters were compared. Precision, accuracy and interferences were noted.

### Preparation of Samples and Reporting of Results

Four water sample concentrates were prepared by dissolving weighed amounts of reagent-grade chemicals in ASTM reagent-grade distilled water to produce accurately-known concentrations of organic and inorganic mercury.

The concentrates were preserved with 0.15% nitric acid, and were checked for stability by repeated analyses over a period of three months. These analyses verified the concentration and stability of each solution. Further confirmation of the true values was achieved with analyses by an independent referee laboratory. The true values are shown in Table 1.

Table 1

True Values for Parameters*

When diluted in distilled water according to instructions, the water samples contained the following concentrations of mercury:

| Sample | Mercury Form | Concentration, µg/liter |
|---|---|---|
| 1 | Mercuric Chloride | 0.34 |
| 2 | Mercuric Chloride | 4.2 |
| 3 | Mercuric Chloride + Phenyl Mercuric Acetate | 3.15 + 3.15 |
| 4 | Phenyl Mercuric Acetate | 4.2 |

*The concentration given are those calculated and added. These are not based on analyses which are used for verification only.

Since dilution of the concentrates renders the acid ineffective as a preservative, the analyst was instructed to add 1.5 ml of redistilled acid/liter in sample make-up.

Study Plan and Analytical Method

The mercury samples were announced in a September 8, 1970 memorandum. Cards were included with the invitation with which laboratories could request samples. On September 28 and 29, 1970, the first series of samples were mailed to requesting laboratories. Since these samples were announced again through the quarterly AQCL Newsletter and by word of mouth, requests for samples were received over the next 12 months. Each requesting laboratory was sent a set(s) of four ampuls, instructions for sample preparation, duplicated report sheets and a statement of true values. Because many laboratories are interested in efficiency of different digestion procedures used to convert organic mercury prior to analysis, the Analytical Quality Control Laboratory requested that data be returned from all laboratories for preparation of an informal report to all participants. A cut-off date of

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September 30, 1971 was set and all data returned to M&PE by that date are included in this report.

The data obtained using the basic EPA Method (acid-permanganate-persulfate oxidation) are combined. Because the many laboratories used almost as many method variations, there was not sufficient data to statistically treat these method results separately. Therefore, all data obtained by methods other than the EPA Method are combined as "Other Method". However, anyone who wishes, can retrieve any segment of data obtained using an other method and make a separate comparison with recoveries by the EPA Method. Each method is specified as clearly as possible without identifying the laboratory. The number of significant figures used are equal to the true values which contain two figures, or to one significant figure if so reported by the laboratory. Any reported "less than" values were accepted but could not be used in the computerized evaluation.

## RESULTS

### Raw Data

The test results are reported by sample in Tables 2, 3, 4, and 5, using a numbering of the laboratories and analysts in the order in which the data were received. For distilled water samples, a simple listing is given of laboratories and analysts with their reported values. For the natural water samples, values determined by difference were reported by each analyst and because spiking 995 ml of natural water with 5 ml of sample concentrate causes a 0.5% dilution change, the reported values for natural waters were reduced by this amount whenever significant. To avoid premature round-off errors in computer calculations four digits were carried in the statistical tables. However, a maximum of two significant figures was used for all final values based on the number of significant figures in the increment values. When values containing only one significant figure were returned by an analyzing laboratory, these figures are reported as received.

It should be noted that the provisional EPA Method as used in this study included acid and permanganate plus potassium persulfate to improve oxidation, but no heating step. However, later data have shown that heating is required to recover methyl mercury chloride from natural waters.

The approved EPA Method now includes an acid-permanganate-persulfate oxidation procedure and heat, prior to reduction, to assure conversion of all organic mercury compounds to ionic form before AA measurement. It is given in Appendix A and is further described in: Kopp, J. F., Longbottom, M. C., and Lobring, L. B., " 'Cold Vapor' Method for the Determination of Mercury," *JAWWA*, Vol. 64, No. 1, January, 1972, pp. 20-25. However, the heating step was not needed to recover 100% of the particular inorganic and organic mercury compounds used in this study.

Because the analytical methods, other than EPA, varied in the kinds and concentration of oxidizing reagent, time and temperature of oxidation, etc., each laboratory was asked to describe its method in detail or to furnish a complete published reference to it. This information is given in Appendix B.

TABLE 2

Average Recoveries of Increment; 0.34 µg of Inorganic Mercury/liter, (Sample 1)
Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 1 | <0.5 | 0.3 | | | Ag wire deposition |
| 2 | | 0.48 | | | Sulfuric, nitric, and perchloric acid reflux |
| 3 | 0.52 | | 0.39 | | Acid permanganate |
| 4 | | 0.2 | | 0.2 | CdS pad |
| 5 | | 0.4 | | 0.3 | Cu wire deposition |
| 6 | 0.33 | 0.34 | 0.35 | | Permanganate |
| 7 | 0.40 | 0.42 | 0.36 | | Acid permanganate |
| 8 | | 0.3 | | 0.4 | Acid permanganate (overnight) |
| 9 | <0.5 | | <0.5 | | |
| 10 | 0.3 | 0.5 | 0.3 | | Acid permanganate |
| 11 | | 1)0.25 | | 0.35 | 1)Acid persulfate at 55 C |
| | | 2)0.45 | | | 2)Acid persulfate at 75 C |
| 12 | 0.3 | 0.5 | 0.3 | 0.3 | Acid permanganate |
| 13 | 0.4 | | 0.4 | | |
| 14 | | | 0.32 | | |
| 15 | 0.38 | 0.31 | | | Acid + heat |
| 16 | 0.4 | | 0.3 | | |
| 17 | 0.25 | | 0.3 | | |
| 18 | | .33 | | | Acid permanganate |
| 19 | 0.30 | | 0.30 | | |
| 20 | | 0.56 | | | Acid, permanganate, and persulfate with heating |
| 21 | <0.5 | <0.5 | | | Acid permangante |
| 22 | <0.5 | | <0.5 | | |
| 23 | 0.35 | | 0.55 | | |
| 24 | 0.35 | | | | |
| 25 | 0.38 | | 0.34 | | |
| 26 | 0.33 | | | | |

TABLE 2 contd.

Average Recoveries of Increment; 0.34 µg of Inorganic Mercury/liter, (Sample 1)
Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 27 | 0.35 | | 0.35 | | |
| 28 | | 1)0.6<br>2)0.8 | | | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 29 | 0.4 | | | | |
| 30 | 0.32 | 0.32 | | | Acid permanganate |
| 31 | | 1)0.40<br>2)0.60 | | 1)0.40<br>2)0.60 | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 32 | 0.2 | | 0 (Sewage Sample) | | |
| 33 | .28 | | | | |
| 34 | 1)<1.0<br>2)<1.0 | 1)<1.0<br>2)<1.0 | 1)<1.0<br>2)<1.0<br>(Tap Water) | 1)<1.0<br>2)<1.0 | 1)Acid permanganate<br>2)Acid permanganate |
| 35 | 0.31 | | | | |
| 36 | | 0.34 | | | Stannous chloride reduction |
| 37 | 0.31 | | | | |
| 39 | | 0.5 | | | Acid permanganate |
| 40 | | 0.0 | | 0.4 | Acid, peroxide, and permanganate |
| 41 | | 0.59 | | | Acid permanganate |
| 42 | | 0.30 | | | Modified DOW |

TABLE 3

Average Recoveries of Increment; 4.2 µg of Inorganic Mercury/liter, (Sample 2) Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 1 | 4.0 | 4.3 | | | Silver wire deposition |
| 2 | | 4.4 | | | Sulfuric, nitric, and perchloric acid reflux |
| 3 | 4.2 | | 3.9 | | Acid permanganate |
| 4 | | 4 | | 3 | CdS pad |
| 5 | | 4.5 | | 4.4 | Copper wire deposition |
| 6 | 3.86 | 3.99 | 3.90 | | Permanganate |
| 7 | 3.81 | 4.2 | 4.1 | | Acid permanganate |
| 8 | | 4.0 | | 4.0 | Acid permanganate (overnight) |
| 9 | 4.5 | | 4.5 | | |
| 10 | 3.8 | 5.1 | 3.0 | | Acid permanganate |
| 11 | | 1)3.55 | | 4.90 | 1)Acid persulfate at 55 C |
| | | 2)4.30 | | | 1)Acid persulfate at 75 C |
| 12 | 3.6 | 3.5 | 3.9 (Tap Water) | 4.0 | Acid permanganate |
| 13 | 4.5 | | 4.2 | | |
| 14 | | | 4.4 | | |
| 15 | 2.0 | 2.0 | | | Acid + heat |
| 16 | 4.3 | | 4.0 | | |
| 17 | 3.4 | | 3.9 | | |
| 18 | | 4.1 | | | Acid permanganate |
| 19 | 4.3 | | 3.7 | | |
| 20 | | 4.1 | | | Acid, permanganate, and persulfate |
| 21 | 3.8 | 3.2 | | | Acid permanganate |
| 22 | 4.2 | | 4.0 | | |
| 23 | 3.50 | | 3.94 | | |
| 25 | 3.1 | | 4.1 | | |

TABLE 3 contd.

Average Recoveries of Increment; 4.2 µg of Inorganic Mercury/liter, (Sample 2) Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 26 | 4.2 | | | | |
| 27 | 4.30 | | 4.30 | | |
| 28 | | 1)3.5<br>2)4.1 | | | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 29 | 4.3 | | | | |
| 30 | 4.3 | 4.1 | | | Acid permanganate |
| 31 | | 1)4.1<br>2)4.1 | | 1)4.6<br>2)4.3 | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 32 | 4.2 | | 2.1 (Sewage Sample) | | |
| 33 | 4.2 | | | | |
| 34 | 1)4.4<br>2)4.2 | 1)4.3<br>2)4.6 | 1)4.4<br>2)5.4 (Tap Water) | 1)4.6<br>2)5.2 | Acid permanganate<br>Acid permanganate |
| 35 | 4.1 | | | | |
| 36 | | 4.1 | | | Stannous chloride reduction |
| 37 | 3.9 | | | | |
| 38 | 3.13 | 1)3.08<br>2)2.72<br>3)3.69 | | | 1)Acid permanganate<br>2)Acid only<br>3)Acid only |
| 39 | | 1.5 | | | Acid permanganate |
| 40 | | 4.0 | | 4.4 | Acid, peroxide, and permanganate |
| 41 | | 4.6 | | | Acid permanganate |
| 42 | | 4.4 | | | Modified DOW |

TABLE 4

Average Recoveries of Increment; 6.3 µg of Inorganic and Organic Mercury/liter (Sample 3)

Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 1 | 6.0 | 5.1 | | | Ag wire deposition |
| 2 | | 6.7 | | | Sulfuric, nitric, and perchloric acid reflux |
| 3 | 6.8 | | 5.0 | | |
| 4 | | 4 | | 6 | CdS pad |
| 5 | | 7.0 | | 7.0 | Cu wire deposition |
| 6 | 6.20 | 3.57 | 5.96 | | Permanganate |
| 7 | 6.0 | 4.6 | 6.6 | | Permanganate |
| 8 | | 4.8 | | 4.8 | Acid permanganate (overnight) |
| 9 | 7.0 | | 7.0 | | |
| 10 | 5.8 | 4.1 | 4.4 | | Permanganate |
| 11 | | 1)5.40 | | 5.40 | 1)Acid persulfate at 55 C |
| | | 2)6.20 | | | 2)Acid persulfate at 75 C |
| 12 | 5.6 | 6.4 | 6.3 (Tap Water) | 6.4 | Acid permanganate |
| 13 | 6.2 | | 4.2 | | |
| 14 | | | 6.2 | | |
| 15 | 6.9 | 5.7 | | | Acid + heat |
| 16 | 6.4 | | 5.4 | | |
| 17 | 5.8 | | 5.6 | | |
| 18 | | 6.3 | | | Acid permanganate |
| 19 | 6.1 | | 5.5 | | |
| 20 | | 6.4 | | | Acid, permanganate, and persulfate |
| 21 | 6.0 | 3.7 | | | Acid permanganate |
| 22 | 6.5 | | 5.8 | | |
| 23 | 5.44 | | 5.13 | | |
| 25 | 6.0 | | 6.8 | | |

TABLE 4 contd.

Average Recoveries of Increment; 6.3 µg of Inorganic and Organic Mercury/liter (Sample 3)

Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 26 | 6.1 | | | | |
| 27 | 6.50 | | 6.50 | | |
| 28 | | 1)3.0<br>2)6.1 | | | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 29 | 8.0 | | | | |
| 30 | 5.6 | 6.2 | | | Acid permanganate |
| 31 | | 1)5.8 1)4.4<br>2)8.7 2)6.9 | | 1)5.6<br>2)8.6 | 1)Acid permanganate (DOW)<br>2)Acid, permanganate + KBr (Modified DOW) |
| 32 | 6.2 | | 1.7 (Sewage Sample) | | |
| 33 | 6.0 | | | | |
| 34 | 1)4.0<br>2)5.2 | 1)3.6<br>2)5.4 | 1)5.9<br>2)7.0 | 1)6.0<br>2)6.3 | 1)Acid permanganate<br>2)Acid permanganate |
| 35 | 6.1 | | | | |
| 36 | 5.9 | | | | |
| 37 | 6.4 | | | | |
| 38 | | 5.33 | | | Acid |
| 39 | | 1.7 | | | Acid permanganate |
| 40 | | 4.9 | | 5.4 | |
| 41 | | 5.9 | | | Acid permanganate Modified DOW |
| 42 | 6.2 | 3.8 | | | |

TABLE 5

Average Recoveries of Increment; 4.2 µg of Organic Mercury/liter, (Sample 4)
Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 1 | 4.2 | 0.8 | | | Ag wire deposition |
| 2 | | 4.8 | | | Sulfuric, nitric and perchloric acid reflux |
| 3 | 4.3 | | 4.1 | | |
| 4 | | 4 | | 4 | CdS pad |
| 5 | | 4.4 | | 4.2 | Cu wire deposition |
| 6 | 4.30 | 0.60 | 3.90 | | Permanganate |
| 7 | 4.3 | 3.0 | 4.4 | | Acid permanganate |
| 8 | | 2.3 | | 3.2 | Acid permanganate (overnight) |
| 9 | 5.5 | | 5.5 | | |
| 10 | 4.2 | 0.7 | 3.5 | | Acid permanganate |
| 11 | | 1)3.70 | | 3.20 | 1)Acid persulfate at 55 C |
| | | 2)4.65 | | | 2)Acid persulfate at 75 C |
| 12 | 4.2 | 4.2 | 4.3 (Tap Water) | 4.6 | Acid permanganate |
| 13 | 4.6 | | 3.8 | | |
| 14 | | | 3.9 | | |
| 15 | 4.7 | 3.9 | | | Acid and heat |
| 16 | 4.2 | | 2.9 | | |
| 17 | 4.0 | | 4.0 | | |
| 18 | | 4.2 | | | Acid permanganate |
| 19 | 4.1 | | 3.6 | | |
| 20 | | 4.4 | | | Acid, permanganate, and persulfate with heating |
| 21 | 4.1 | 0.6 | | | Acid permanganate |
| 22 | 4.3 | | 4.0 | | |
| 23 | 3.50 | | 3.31 | | |
| 25 | 4.3 | | 4.5 | | |

TABLE 5 contd.

Average Recoveries of Increment; 4.2 µg of Organic Mercury/liter, (Sample 4)
Concentration, µg/liter

| Laboratory Code | Distilled Water | | Natural Water | | Description of Other Method |
|---|---|---|---|---|---|
| | EPA Method | Other Method | EPA Method | Other Method | |
| 26 | 4.3 | | | | |
| 27 | 4.10 | | 4.10 | | |
| 28 | | 1)0.7<br>2)3.7 | | | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 29 | 5.0 | | | | |
| 30 | 4.1 | 4.4 | | | Acid permanganate |
| 31 | | 1)1.0<br>2)4.6 | | 1)0.6<br>2)4.1 | 1)Acid permanganate (DOW)<br>2)Acid permanganate + KBr (Modified DOW) |
| 32 | 3.8 | | 0.2 (Sewage Sample) | | |
| 33 | 4.2 | | | | Acid permanganate |
| 34 | 1)1.0<br>2)3.0 | 1)<1.0<br>2) 2.9 | 1)4.4<br>2)4.6<br>(Tap Water) | 1)3.7<br>2)4.7 | 1)Acid permanganate<br>2)Acid permanganate |
| 35 | 4.2 | | | | |
| 36 | 3.3 | | | | |
| 37 | 4.2 | | | | |
| 38 | 2.58 | 1)2.81<br>2)2.64<br>3)2.89 | | | 1)Acid permanganate<br>2)Acid<br>3)Acid |
| 39 | | 2.8 | | | Acid permanganate |
| 40 | | 3.9 | | 0.7 | Acid, peroxide, and permanganate |
| 41 | | 5.4 | | | Acid permanganate |
| 42 | 4.1 | 0.7 | | | Modified DOW |

## TREATMENT OF DATA

### Statistical Summary

Complete statistical summaries are given in pages 18 thru 33. Each sample is discussed in turn with the data displayed by type of water sample and method of analysis. A statistical evaluation is provided for each concentration with each set of sample-test conditions.

In addition to the statistical measurements, all data are ranked in ascending order and are presented in a histogram using $\sqrt{n}$ cell divisions. Each X in the histogram represents one analytical result for 1-15 values/cell. When more than 15 values occur per cell, only 15 X's are printed and the number of values included in the cell is printed at the base of the cell.

With the exception of accuracy, the statistical parameters: *number of values, true values, mean, range, variance, standard deviation, 95% confidence limit,* and *relative deviation* (coefficient of variation) are based on all of the data received, without rejection. *Accuracy* is based on retained data, that is the data remaining after rejection of outliers.

### Rejection of Outliers

To determine the accuracy of each method, it was necessary to remove those extreme values which had only a small chance of validity and which would make a significant change in the reported accuracy. These values were probably caused by gross instrumental, chemical or human error and were rejected by applying the two-tail *t-test* to all values at a 99% probability level; that is, with a 99 to 1 assurance that the data rejected were invalid and should be rejected. Each rejected value is indicated in the statistical summaries by laboratory and analyst with a capital letter "R", after the value.

A greater spread of data round the true value causes rejection of fewer outliers because a larger standard deviation in the denominator of the *t-test* reduces the calculated *t* value and fewer extreme values are rejected as outliers. Contrariwise, with better accuracy and precision, the *t-test* is more powerful and more outliers are rejected. However, the data rejected in either case are true outliers and laboratories reporting such values should carefully review procedures for the cause of inaccuracy. A glossary of the statistical terms used in this study is included at the end of this report on pages 57 and 58.

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 1 INCREMENT = 0.34 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 21 | RANGE | 0.32000 | COEF. VAR. | 0.19541 |
| TRUE VAL. | 0.34 | VARIANCE | 0.00443 | SKEWNESS | 0.45532 |
| MEAN | 0.34095 | STD. DEV. | 0.06662 | NO. OF CELLS | 4 |
| MEDIAN | 0.33000 | CONF. LIM. | 0.13058 (95 PCT) | | |
| ACCURACY | 0.28003 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.20 | 0.2000 | 2 | XX |
| 0.25 | 0.3066 | 12 | XXXXXXXXXXXX |
| 0.28 | 0.4133 | 6 | XXXXXX |
| 0.30 | 0.5199 | 1 | X |
| 0.30 | | | |
| 0.30 | | | |
| 0.31 | | | |
| 0.31 | | | |
| 0.32 | | | |
| 0.33 | | | |
| 0.33 | | | |
| 0.35 | | | |
| 0.35 | | | |
| 0.35 | | | |
| 0.38 | | | |
| 0.38 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.52 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 1 INCREMENT = 0.34 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 13 | RANGE | 0.25000 | COEF. VAR. | 0.19767 |
| TRUE VAL. | 0.34 | VARIANCE | 0.00480 | SKEWNESS | 1.92644 |
| MEAN | 0.35076 | STD. DEV. | 0.06933 | NO. OF CELLS | 3 |
| MEDIAN | 0.34000 | CONF. LIM. | 0.13590 (95 PCT) | | |
| ACCURACY | 3.16737 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.30 | 0.3000 | 10 | XXXXXXXXXX |
| 0.30 | 0.4250 | 2 | XX |
| 0.30 | 0.5500 | 1 | X |
| 0.30 | | | |
| 0.30 | | | |
| 0.32 | | | |
| 0.34 | | | |
| 0.35 | | | |
| 0.35 | | | |
| 0.36 | | | |
| 0.39 | | | |
| 0.40 | | | |
| 0.55 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 1 INCREMENT = 0.34 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 24 | RANGE | 0.80000 | COEF. VAR. | 0.40046 |
| TRUE VAL. | 0.34 | VARIANCE | 0.02679 | SKEWNESS | -0.01854 |
| MEAN | 0.40874 | STD. DEV. | 0.16368 | NO. OF CELLS | 4 |
| MEDIAN | 0.40000 | CONF. LIM. | 0.32082 (95 PCT) | | |
| ACCURACY | 20.22049 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.00 | 0.0000 | 1 | X |
| 0.20 | 0.2666 | 12 | XXXXXXXXXXXX |
| 0.25 | 0.5333 | 10 | XXXXXXXXXX |
| 0.30 | 0.8000 | 1 | X |
| 0.30 | | | |
| 0.30 | | | |
| 0.31 | | | |
| 0.32 | | | |
| 0.33 | | | |
| 0.34 | | | |
| 0.36 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.42 | | | |
| 0.45 | | | |
| 0.48 | | | |
| 0.50 | | | |
| 0.50 | | | |
| 0.50 | | | |
| 0.56 | | | |
| 0.59 | | | |
| 0.60 | | | |
| 0.60 | | | |
| 0.80R | | | |

R REJECTED DATA

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 1 INCREMENT = 0.34 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 8 | RANGE | 0.39999 | COEF. VAR. | 0.31540 |
| TRUE VAL. | 0.34 | VARIANCE | 0.01352 | SKEWNESS | 0.67914 |
| MEAN | 0.36874 | STD. DEV. | 0.11630 | NO. OF CELLS | 2 |
| MEDIAN | 0.37500 | CONF. LIM. | 0.22795 (95 PCT) | | |
| ACCURACY | 8.45584 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.20 | 0.2000 | 4 | XXXX |
| 0.30 | 0.6000 | 4 | XXXX |
| 0.30 | | | |
| 0.35 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.40 | | | |
| 0.60 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 2 INCREMENT = 4.2 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 28 | RANGE | 2.50000 | COEF. VAR. | 0.13604 |
| TRUE VAL. | 4.2 | VARIANCE | 0.28664 | SKEWNESS | -1.92003 |
| MEAN | 3.93535 | STD. DEV. | 0.53539 | NO. OF CELLS | 5 |
| MEDIAN | 4.15000 | CONF. LIM. | 1.04937 (95 PCT) | | |
| ACCURACY | -6.30110 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 2.0R | 2.0000 | 1 | X |
| 3.1 | 2.6250 | 0 | |
| 3.1 | 3.2500 | 4 | XXXX |
| 3.4 | 3.8750 | 9 | XXXXXXXXX |
| 3.5 | 4.5000 | 14 | XXXXXXXXXXXXX |
| 3.6 | | | |
| 3.8 | | | |
| 3.8 | | | |
| 3.8 | | | |
| 3.8 | | | |
| 3.9 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.4 | | | |
| 4.5 | | | |
| 4.5 | | | |

R REJECTED DATA

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 2 INCREMENT = 4.2 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 18 | RANGE | 3.30000 | COEF. VAR. | 0.16576 |
| TRUE VAL. | 4.2 | VARIANCE | 0.43646 | SKEWNESS | -0.95187 |
| MEAN | 3.98555 | STD. DEV. | 0.66065 | NO. OF CELLS | 4 |
| MEDIAN | 4.00000 | CONF. LIM. | 1.29487 (95 PCT) | | |
| ACCURACY | -5.10587 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 2.1R | 2.1000 | 1 | X |
| 3.0 | 3.2000 | 2 | XX |
| 3.7 | 4.3000 | 14 | XXXXXXXXXXXXX |
| 3.9 | 5.3999 | 1 | X |
| 3.9 | | | |
| 3.9 | | | |
| 3.9 | | | |
| 3.9 | | | |
| 4.0 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.2 | | | |
| 4.3 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.5 | | | |
| 5.4 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 2 INCREMENT = 4.2 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 29 | RANGE | 3.59999 | COEF. VAR. | 0.19871 |
| TRUE VAL. | 4.2 | VARIANCE | 0.58928 | SKEWNESS | -1.48013 |
| MEAN | 3.86309 | STD. DEV. | 0.76764 | NO. OF CELLS | 5 |
| MEDIAN | 4.10000 | CONF. LIM. | 1.50459 (95 PCT) | | |
| ACCURACY | -8.02143 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 1.5R | 1.5000 | 1 | X |
| 2.0R | 2.4000 | 2 | XX |
| 2.7 | 3.2999 | 6 | XXXXXX |
| 3.0 | 4.1999 | 19 | XXXXXXXXXXXXXXX |
| 3.2 | 5.0999 | 1 | X |
| 3.5 | | | |
| 3.5 | | | |
| 3.5 | | | |
| 3.6 | | | |
| 3.9 | | | |
| 4.0 | | | |
| 4.0 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.2 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.5 | | | |
| 4.6 | | | |
| 4.6 | | | |
| 5.1 | | | |

R REJECTED DATA

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 2 INCREMENT = 4.2 µg/liter, INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 10 | RANGE | 2.20000 | COEF. VAR. | 0.13790 |
| TRUE VAL. | 4.2 | VARIANCE | 0.35822 | SKEWNESS | -0.89451 |
| MEAN | 4.33999 | STD. DEV. | 0.59851 | NO. OF CELLS | 3 |
| MEDIAN | 4.40000 | CONF. LIM. | 1.17309 (95 PCT) | | |
| ACCURACY | 3.33327 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 3.0 | 3.0000 | 1 | X |
| 4.0 | 4.1000 | 7 | XXXXXXX |
| 4.0 | 5.1999 | 2 | XX |
| 4.3 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.6 | | | |
| 4.6 | | | |
| 4.9 | | | |
| 5.2 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 3 INCREMENT = 6.3 µg/liter, ORGANIC + INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 28 | RANGE | 4.00000 | COEF. VAR. | 0.11151 |
| TRUE VAL. | 6.3 | VARIANCE | 0.46351 | SKEWNESS | -0.25732 |
| MEAN | 6.10499 | STD. DEV. | 0.68081 | NO. OF CELLS | 5 |
| MEDIAN | 6.10000 | CONF. LIM. | 1.33440 (95 PCT) | | |
| ACCURACY | -3.09527 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 4.0R | 4.0000 | 1 | X |
| 5.2 | 5.0000 | 2 | XX |
| 5.4 | 6.0000 | 21 | XXXXXXXXXXXXXXX |
| 5.6 | 7.0000 | 3 | XXX |
| 5.6 | 8.0000 | 1 | X |
| 5.8 | | | |
| 5.8 | | | |
| 5.9 | | | |
| 6.0 | | | |
| 6.0 | | | |
| 6.0 | | | |
| 6.0 | | | |
| 6.0 | | | |
| 6.1 | | | |
| 6.1 | | | |
| 6.1 | | | |
| 6.2 | | | |
| 6.2 | | | |
| 6.2 | | | |
| 6.2 | | | |
| 6.4 | | | |
| 6.4 | | | |
| 6.5 | | | |
| 6.5 | | | |
| 6.8 | | | |
| 6.9 | | | |
| 7.0 | | | |
| 8.0 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AOCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 3 INCREMENT = 6.3 µg/liter, ORGANIC + INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 18 | RANGE | 5.30000 | COEF. VAR. | 0.22676 |
| TRUE VAL. | 6.3 | VARIANCE | 1.61873 | SKEWNESS | -1.62836 |
| MEAN | 5.61055 | STD. DEV. | 1.27229 | NO. OF CELLS | 4 |
| MEDIAN | 5.85000 | CONF. LIM. | 2.49369 (95 PCT) | | |
| ACCURACY | -10.94361 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 1.7R | 1.7000 | 1 | X |
| 4.2 | 3.4666 | 1 | X |
| 4.4 | 5.2333 | 9 | XXXXXXXXX |
| 5.0 | 7.0000 | 7 | XXXXXXX |
| 5.1 | | | |
| 5.4 | | | |
| 5.5 | | | |
| 5.6 | | | |
| 5.8 | | | |
| 5.9 | | | |
| 5.9 | | | |
| 6.2 | | | |
| 6.3 | | | |
| 6.5 | | | |
| 6.6 | | | |
| 6.8 | | | |
| 7.0 | | | |
| 7.0 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 3 INCREMENT = 6.3 ug/liter, ORGANIC + INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 29 | RANGE | 7.00000 | COEF. VAR. | 0.27779 |
| TRUE VAL. | 6.3 | VARIANCE | 2.11163 | SKEWNESS | -0.14497 |
| MEAN | 5.23102 | STD. DEV. | 1.45314 | NO. OF CELLS | 5 |
| MEDIAN | 5.40000 | CONF. LIM. | 2.84816 (95 PCT) | | |
| ACCURACY | -16.96777 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 1.7R | 1.7000 | 1 | X |
| 3.0 | 3.4499 | 7 | XXXXXXX |
| 3.5 | 5.1999 | 11 | XXXXXXXXXXX |
| 3.6 | 6.9499 | 9 | XXXXXXXXX |
| 3.7 | 8.6999 | 1 | X |
| 3.8 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.4 | | | |
| 4.6 | | | |
| 4.8 | | | |
| 4.9 | | | |
| 5.1 | | | |
| 5.3 | | | |
| 5.4 | | | |
| 5.4 | | | |
| 5.7 | | | |
| 5.8 | | | |
| 5.9 | | | |
| 6.1 | | | |
| 6.2 | | | |
| 6.2 | | | |
| 6.3 | | | |
| 6.4 | | | |
| 6.4 | | | |
| 6.7 | | | |
| 6.9 | | | |
| 7.0 | | | |
| 8.7 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 3 INCREMENT = 6.3 µg/liter, ORGANIC + INORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 10 | RANGE | 3.79999 | COEF. VAR. | 0.17229 |
| TRUE VAL. | 6.3 | VARIANCE | 1.12277 | SKEWNESS | 1.16776 |
| MEAN | 6.14999 | STD. DEV. | 1.05961 | NO. OF CELLS | 3 |
| MEDIAN | 6.00000 | CONF. LIM. | 2.07683 (95 PCT) | | |
| ACCURACY | -2.38097 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 4.8 | 4.8000 | 4 | XXXX |
| 5.4 | 6.6999 | 5 | XXXXX |
| 5.4 | 8.6000 | 1 | X |
| 5.6 | | | |
| 6.0 | | | |
| 6.0 | | | |
| 6.3 | | | |
| 6.4 | | | |
| 7.0 | | | |
| 8.6 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 4 INCREMENT = 4.2 µg/liter, ORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 29 | RANGE | 4.50000 | COEF. VAR. | 0.19789 |
| TRUE VAL. | 4.2 | VARIANCE | 0.63394 | SKEWNESS | -1.97527 |
| MEAN | 4.02344 | STD. DEV. | 0.79620 | NO. OF CELLS | 5 |
| MEDIAN | 4.20000 | CONF. LIM. | 1.56056 (95 PCT) | | |
| ACCURACY | -4.20372 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 1.OR | 1.0000 | 1 | X |
| 2.5 | 2.1250 | 1 | X |
| 3.0 | 3.2500 | 4 | XXXX |
| 3.3 | 4.3750 | 21 | XXXXXXXXXXXXXXX |
| 3.5 | 5.5000 | 2 | XX |
| 3.8 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.2 | | | |
| 4.2 | | | |
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| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.3 | | | |
| 4.6 | | | |
| 4.7 | | | |
| 5.0 | | | |
| 5.5 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
EPA METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 4 INCREMENT = 4.2 µg/liter, ORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 18 | RANGE | 5.30000 | COEF. VAR. | 0.27855 |
| TRUE VAL. | 4.2 | VARIANCE | 1.14055 | SKEWNESS | -2.14235 |
| MEAN | 3.83388 | STD. DEV. | 1.06796 | NO. OF CELLS | 4 |
| MEDIAN | 4.00000 | CONF. LIM. | 2.09321 (95 PCT) | | |
| ACCURACY | -8.71698 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.2R | 0.2000 | 1 | X |
| 2.9 | 1.9666 | 0 | |
| 3.3 | 3.7333 | 16 | XXXXXXXXXXXXXXX |
| 3.5 | 5.5000 | 1 | X |
| 3.6 | | | |
| 3.8 | | | |
| 3.9 | | | |
| 3.9 | | | |
| 4.0 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.1 | | | |
| 4.3 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.5 | | | |
| 4.6 | | | |
| 5.5 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM DISTILLED WATER

AMPUL 4 INCREMENT = 4.2 µg/liter, ORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 28 | RANGE | 4.80000 | COEF. VAR. | 0.50731 |
| TRUE VAL. | 4.2 | VARIANCE | 2.35456 | SKEWNESS | -0.46796 |
| MEAN | 3.02464 | STD. DEV. | 1.53445 | NO. OF CELLS | 5 |
| MEDIAN | 3.35000 | CONF. LIM. | 3.00753 (95 PCT) | | |
| ACCURACY | -27.98476 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.6 | 0.6000 | 7 | XXXXXXX |
| 0.6 | 1.7999 | 1 | X |
| 0.7 | 3.0000 | 6 | XXXXXX |
| 0.7 | 4.1999 | 13 | XXXXXXXXXXXX |
| 0.7 | 5.3999 | 1 | X |
| 0.8 | | | |
| 1.0 | | | |
| 2.3 | | | |
| 2.6 | | | |
| 2.8 | | | |
| 2.8 | | | |
| 2.8 | | | |
| 2.9 | | | |
| 3.0 | | | |
| 3.7 | | | |
| 3.7 | | | |
| 3.9 | | | |
| 3.9 | | | |
| 4.0 | | | |
| 4.2 | | | |
| 4.2 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.4 | | | |
| 4.6 | | | |
| 4.6 | | | |
| 4.8 | | | |
| 5.4 | | | |

R REJECTED DATA

METHOD & PERFORMANCE EVALUATION, AQCL
PRELIMINARY STUDY, ANALYSES FOR MERCURY IN WATER

ALL DATA, ALL LABORATORIES
OTHER METHOD
RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 4 INCREMENT = 4.2 µg/liter, ORGANIC MERCURY

| | | | | | |
|---|---|---|---|---|---|
| N | 10 | RANGE | 4.10000 | COEF. VAR. | 0.44969 |
| TRUE VAL. | 4.2 | VARIANCE | 2.20222 | SKEWNESS | -1.09921 |
| MEAN | 3.29999 | STD. DEV. | 1.48398 | NO. OF CELLS | 3 |
| MEDIAN | 3.85000 | CONF. LIM. | 2.90861 (95 PCT) | | |
| ACCURACY | -21.42860 | PCT RELATIVE ERROR, RETAINED DATA | | | |

| DATA IN ASCENDING ORDER | MIDPOINT | FREQ | HISTOGRAM |
|---|---|---|---|
| 0.6 | 0.6000 | 2 | XX |
| 0.7 | 2.6500 | 2 | XX |
| 3.2 | 4.6999 | 6 | XXXXXX |
| 3.2 | | | |
| 3.7 | | | |
| 4.0 | | | |
| 4.1 | | | |
| 4.2 | | | |
| 4.6 | | | |
| 4.7 | | | |

R REJECTED DATA

## DISCUSSION

### 0.34 µg/liter, Inorganic Mercury

At the 0.34 µg inorganic mercury/liter level, the EPA Method was more accurate and more precise in both distilled water and natural water. Accuracies of 0.3% positive bias for EPA Method and 20% positive bias for the Other Method were found in distilled water and 3% and 8.5% positive bias in the natural waters for these two methods, respectively. Differences in precision were similar in distilled and natural waters with 20% and 40% relative deviation for the EPA and Other Method in distilled water, and 20% and 32% relative deviation in natural waters for the two methods, respectively.

### 4.2 µg/liter, Inorganic Mercury

At this 4.2 µg/liter level, the EPA and Other Method showed low bias values of 6% and 8% in distilled water and -5% and +3% in natural waters. The precision values were similar for the two methods with relative deviations of 14% and 20% in distilled water for the EPA and Other Method, respectively, and 17% and 14% in natural waters for the two methods, respectively.

### 6.3 µg/liter of Organic and Inorganic Mercury

This higher level of mercury made up of equal amounts of organic and inorganic mercury showed negative bias of 3% and 17% in distilled water for the EPA and Other Methods, respectively. However, in natural water, the negative bias values were reversed with 11% for the EPA Method and 2% for the Other Method.

Likewise, precision as relative deviation was 11% for the EPA Method and 28% for the Other Method in distilled water. In natural waters the EPA Method showed a 23% deviation while the Other Method showed a 17% deviation.

### 4.2 µg/liter, Organic Mercury

The presence of only organic mercury as phenyl mercuric acetate in the fourth sample provided a rigorous test of the oxidation step in the methods

since no mercury was measurable without conversion. In distilled water, the results showed a negative bias of 4% for the EPA Method and 28% for the Other Method, and relative deviations of 20% and 51% for the EPA and Other Methods, respectively.

In the natural water samples the results showed negative bias of 9% for the EPA Method and 21% for the Other Method, and relative deviations of 28% and 45% for the EPA and Other Methods, respectively.

This study was not intended to demonstrate the superiority of the EPA Method for total mercury over all other methods. However, the complete variety of methods applied in this study has forced an evaluation only of the EPA Method and other methods as a group. The reader is urged to compare recoveries by each of the methods in Tables 2, 3, 4, and 5. He will note that almost all methods used did recover inorganic mercury rather completely.

However, there was a divergence of results from the Other Method, with samples containing organic mercury, into those which could and those which could not recover the added levels. In Table 5 reporting recoveries of 4.2 µg/liter of organic mercury, the copper wire deposition method of laboratory 5, the acid permanganate of laboratory 12 and the acid permanganate and persulfate of laboratory 20 obtained very good recovery from distilled water. Laboratories 5 and 12 repeated their good recovery of organic mercury in natural waters and were joined by laboratories 31 and 34.

Table 5 shows examples of poor recovery from distilled water samples where laboratories 1, 6, 10, 21, and 42 had minimal recovery with their own method and very good recovery with the EPA Method.

## CONCLUSIONS

This preliminary study on measurement of organic and/or inorganic mercury in distilled and natural waters showed that problems of level of mercury and sample substrate (distilled vs. natural water) were not as significant as the form of the mercury tested.

At the 0.34 - 4.2 µg/liter level of inorganic mercury with one exception the EPA and Other Method showed similar levels of accuracy and precision for both the distilled and natural water samples containing 0.34 or 4.2 µg of inorganic mercury/liter. As expected, when the mercury level was less than 1 µg/liter, the results showed a greater imprecision than at the 4.2 µg/liter level.

At the 6.3 µg/liter level of organic/inorganic mercury containing equal amounts of organic and inorganic mercury, the two methods reversed accuracies and precision in distilled and natural waters. The EPA Method had better accuracy and precision with the distilled water sample, -3% and 11% respectively than in the natural waters where it had a -11% bias and 23% deviation respectively. Conversely, the Other Method showed a negative 17% bias and 28% deviation in distilled water and a negative 2% bias and 17% deviation in the natural waters.

Despite the similar accuracy and precision values shown by the two methods with Sample 3 which contained equal amounts of organic and inorganic mercury, the methods differed significantly with Sample 4 which contained only organic mercury. The EPA Method had a -4% bias in distilled water and a 9% bias in natural water while the Other Method had a -28% bias in distilled water and a -21% in natural water. Likewise, the relative deviation of the EPA Method was 20 and 28% in the distilled and natural water while the Other Method had a relative deviation of 51 and 45% respectively for the distilled and natural water samples.

The performances of the EPA Method and Other Method in recovery of organic and inorganic mercury from distilled and natural water samples have shown that:

1. The EPA Method was more precise with three of the four inorganic mercury samples and three of the four of the samples containing organic mercury.
2. Both methods showed a limited and variable bias with the two inorganic mercury samples and a larger and consistently negative bias with the samples containing organic mercury.

If water samples contain mercury in organic form, a method involving a vigorous digestion step such as that in the EPA Method should be used to insure good recovery.

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# APPENDIX A

## EPA Method for Mercury in Water, April 1972

*(Note: Heating step, 8.1, was not included in EPA Method evaluated in this study)*

April, 1972

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MERCURY IN WATER

(Cold Vapor Technique)

STORET NO.
Total: 71900
Dissolved: 71890

1. Scope and Application

1.1 This method is applicable to surface waters, saline waters, wastewaters, effluents, and domestic sewage.

1.2 In addition to inorganic forms of mercury, organic mercurials may also be present in an effluent or surface water sample. These organomercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl m rcuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organomercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 µg Hg/l can be achieved; concentrations below this level should be reported as <0.2 (see Appendix 11.2).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection[1]. If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on the recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate

reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer*: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL - 22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. x 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter x 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter

*Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" x 3/4" diameter tube containing 20 grams of magnesium perchlorate (see Note 1.) The apparatus is assembled as shown in the accompanying diagram.

NOTE 1: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 1.0 N: Dilute 28.0 ml of conc. sulfuric acid to 1.0 liter.

6.1.2 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content.

NOTE 2: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continously during use.

NOTE 3: Stannous chloride and hydroxylamine hydrochloride may also be used.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in distilled water and dilute to 100.0 ml.

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 grams of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 grams of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 grams of mercuric chloride in 75 ml of distilled water. Add 10 ml of concentrated nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 µg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of concentrated sulfuric acid and 2.5 ml of nitric acid to each bottle.

Add 15 ml of $KMnO_4$ solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride - hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% $H_2SO_4$

b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Transfer 100 ml or an aliquot diluted to 100 ml containing not more than 1.0 µg of mercury to a 300 ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of nitric acid mixing after each addition. Add 15 ml of potassium permanganate solution to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution if necessary until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride - hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu gHg/l = \frac{\mu g\ Hg\ \text{in aliquot}}{} \times \frac{1000}{\text{volume of aliquot}}$$

9.3 Report mercury concentrations as follows:

Below 0.2 µg/l, <0.2; between 1 and 10 µg/l, one decimal; above 10 µg/l, whole numbers.

10. Precision and Accuracy

10.1 Using an Ohio River composite sample with a background mercury concentration of 0.35 µg/l, spiked with concentrations of 1, 3 and 4

µg/1, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, the AQC Laboratory has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows:

If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.25 µg/1 the standard deviations were ±0.027, ±0.006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

References

1. Wallace, R.A., Fulkerson, W., Shults, W.D., and Lyon, W.S., "Mercury in the Environment - The Human Element", Oak Ridge National Laboratory, ORNL - NSF - EP - 1. January, 1971, Page 31.

2. Hatch, W.R., and Ott, W.L., "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry", Anal. Chem. 40, 2085 (1968).

3. Brandenberger, H. and Bader, H., "The Determination of Nanogram Levels of Mercury in Solution by a Flameless Atomic Absorption Technique", Atomic Absorption Newsletter, 6, 101 (1967).

4. Brandenberger, H. and Bader, H., "The Determination of Mercury by Flameless Atomic Absorption II. A Static Vapor Method", Atomic Absorption Newsletter, 7, 53 (1968).

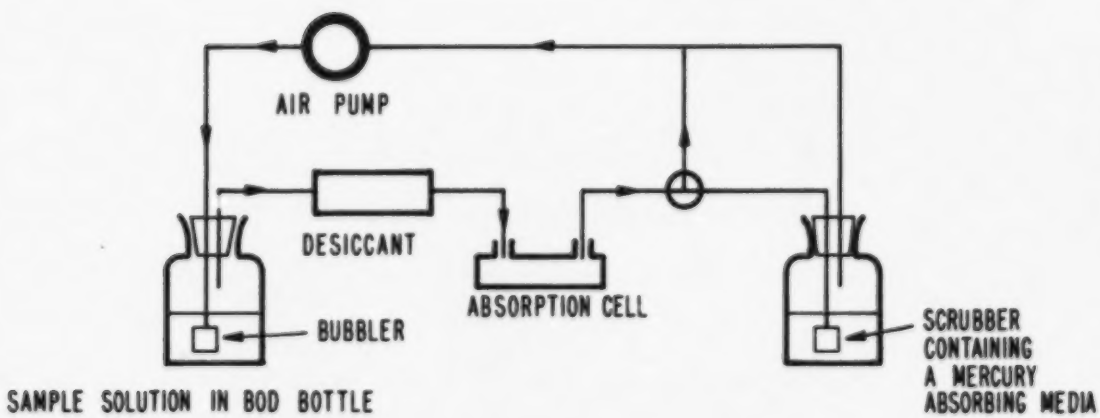


FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.

# APPENDIX B

Details on the Other Method (non-EPA)
Used for Mercury Analyses in this Study

Details of the Other Method (non-EPA) Used for Mercury Analysis in this Study

| Laboratory Designation | Digestion Steps Used in Other Method, Details, and Reference |
|---|---|
| 1 | Silver-Wire Method: Fishman, J. J., *Anal. Chem.*, 42, 1462 (1970). |
| 2 | To sample, add 25 ml 18 N sulfuric acid, 20 ml 7 N nitric acid and 1 ml sodium molybdate solution (2% W/V). Heat for one hour. Cool, add 20 ml (1 + 1) nitric acid-perchloric acid. Boil vigorously till white fumes appear. Heat for another 10 minutes, cool, add 10 ml water, boil again for 10 minutes, cool bring to volume. Source: Massachusetts Division of Fisheries and Game Field Headquarters Westborough, Massachusetts 01581 |
| 4 | Mercury is precipitated from the sample by cadmium sulfide followed by emission spectrographic arc excitation of the mercury in the precipitate. Powdered copper metal is added to samples suspected of containing organo-mercury compounds to reduce the mercury to the metallic form. Source: E. I. du Pont de Nemours & Co. (Inc.) Savannah River Plant Aiken, South Carolina 29801 |
| 5 | Electrodeposition of mercury onto copper wire coil as described in: Brandenberger and Bader, *Atomic Absorption Newsletter*, 6, 101, (1967). |
| 6 | $KMnO_4$ oxidant for five minutes. No other reference. |
| 7 | EPA method without persulfate. |
| 8 | To a 100 ml sample, add 10 ml 18 N sulfuric acid, 5 ml 7 N nitric, 2 ml of 4% potassium permanganate. Let stand overnight. |
| 10 | To a 100 ml sample, add 10 ml 18 N sulfuric acid, 5 ml 7 N nitric acid and 5 ml of 4% potassium permanganate. Mix; then neutralize. |

Details on the Other Method (non-EPA) Used for Mercury Analysis in this Study contd.

| Laboratory Designation | Digestion Steps Used in Other Method, Details, and Reference |
|---|---|
| 11 | To a 100 ml sample, add 2-1/2 ml acid-persulfate (2:1 V/W). Digest on shaking water bath at 55 C for one hour. Cool to R. T., add 5% W/V potassium permanganate in 1 ml increments until color holds for 10 minutes. |
| 12 | Nitric acid-permanganate digestion described in: Rolf, A. C., Russell, F. R., and Wilkinson, N. T., *The Analyst*, 80, 523, (1955). |
| 15 | To a 100 ml sample add 25 ml nitric acid, heat gently for 30 minutes<br><br>Source: Texas A & M University<br>Agricultural Analytical Services<br>College Station, Texas 77843 |
| 18 | Samples digested at 50 - 60 C with sulfuric acid and oxidize with permanganate.<br><br>Source: Uthe, J. F., Armstrong, F. A. J., and Stainton, M. P., *J. of the Fisheries Research Board of Canada*, 27, 805, (1970). |
| 20 | EPA procedure modified: sulfuric acid: nitric acid (20: 10 ml), 10 ml potassium persulfate, 15 ml potassium permanganate, heat for four hours at 50 C.<br><br>Source: Surveillance and Analysis Division, EPA<br>Technical Support Branch<br>620 Central Avenue<br>Alameda, California 94501 |
| 21 | Sulfuric acid-potassium permanganate digestion. No further reference. |
| 28 | To a 50 ml sample add 1 ml of 1:4 sulfuric acid and 1 ml of 4% potassium permanganate. Heat to boiling for few seconds, allow to cool.<br><br>Source: Dow Method CAS-AM-70.13, June 22, 1970, revised.<br>Chlorine Institute Pamphlet M1R-104, No. 3, (1970). |

Details on the Other Method (non-EPA) Used for Mercury Analysis in this Study contd.

| Laboratory Designation | Digestion Steps Used in Other Method, Details, and Reference |
|---|---|
| 30 | Add 10 ml 7 N nitric acid, 25 ml 18 N sulfuric acid and cool. Add 5% potassium permanganate until pink color persists.<br><br>Source: Hatch, W. R. and Ott, W. L., *Analytical Chemistry*, 40, 2085 (1968). |
| 31 | a) Dow procedure as in 28.<br>b) Dow procedure modified by addition of one ml of 10% potassium bromide after the acid and permanganate. Sample allowed to set for one minute before boiling.<br><br>Source: Diamond Shamrock Chemical Company<br>Sheffield, Alabama 35660 |
| 34 | To a 100 ml sample add 10 ml of 18 N sulfuric acid, 5 ml of 7 N nitric acid and 5 ml of 4% W/V potassium permanganate. Modification from Hatch and Ott, reference 30. |
| 36 | To a 5.0 ml sample add 0.5 ml of 5% stannous chloride in 1 N hydrochloric acid.<br><br>Source: Applications Laboratory<br>Instrumentation Laboratory, Inc.<br>Lexington, Massachusetts 02173 |
| 38 | a) To a 10 ml, diluted sample add 10 ml sulfuric acid and 2 ml 5% potassium permanganate. Digest 15 minutes at 90 C then cool.<br><br>b) To a 5 ml, diluted sample add 10 ml nitric acid, digest for 1-1/2 hours at 75 C and 1-1/2 hours at 90 C, cool.<br><br>Measurement using a Beckman DB-G spectrophotometer and a 62.5 cm cell.<br><br>Source: University of Illinois<br>Agronomy Department<br>Urbana-Champaign Campus<br>Urbana, Illinois 61801 |

Details on the Other Method (non-EPA) Used for Mercury Analysis in this Study contd.

| Laboratory Designation | Digestion Steps Used in Other Method, Details, and Reference |
|---|---|
| 39 | To a one-liter sample, add 10 ml of 1 + 1 sulfuric acid and 5 ml of aqueous 2% W/V potassium permanganate. Mix well and let stand 20 hours at room temperature.<br><br>Source: Omang, S., *Anal. Chim Acta*, 53, 415 (1971). |
| 40 | Add 20-30 ml sulfuric acid to sample and reflux on a steam bath with agitation for 30 minutes. Cool to room temperature. Add 50% hydrogen peroxide in 1/2 - 1 ml portions with vigorous mixing. After decomposition is complete, add 5 ml portions of permanganate slowly until color persists for 15 minutes.<br><br>Source: Kimura, Y. and Miller, V., *Anal. Chim Acta*, 27, 325-331 (1962). |
| 41 | To a 100 ml sample add potassium permanganate until a pink color is maintained. 20 ml of 2:1 sulfuric and nitric acid added and sample digested for 24 hours.<br><br>Source: Water Quality Control Research Laboratory<br>Stanford University<br>Civil Engineering Department<br>Palo Alto, California 94305 |
| 42 | Modified DON procedure.<br><br>To a 50 ml sample add 1 ml 4% $KMnO_4$, boil 2 seconds<br><br>Source: Westvaco Corporation<br>Westvaco Research Center<br>Laurel, Maryland 20810 |

## GLOSSARY OF TERMS

The statistical measurements used in method study reports of the Analytical Quality Control Laboratory, are defined as follows:

*Accuracy* as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$\text{R. E., \%} = \frac{X_{true} - \overline{X}}{X_{true}} \times 100$$

*Confidence Limit* (95%). The range of values within which a single analysis will be included, 95% of the time.

$$95\%\ \text{C. L.} = \overline{X} \pm 1.96\sigma$$

*Mean.* The arithmetic mean of reported values, the average.

$$\overline{X} = \frac{\Sigma X}{n}$$

*Median.* Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

*n.* The number of sets of values or analysts reported in a study.

*Range.* The difference between the lowest and highest values reported for a sample.

*Relative Deviation* (Coefficient of Variation). The ratio of the standard deviation, $\sigma$, of a set of numbers to their mean, $\overline{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data to the size of the numbers so that deviations between levels of values can be compared.

$$\text{R. D.} = 100\,\frac{\sigma}{\overline{X}}$$

*Skewness (k).* A pure number, positive or negative, which indicates the lack of symmetry in a distribution. For example, $k$ is positive if the distribution tails to the right and negative if the distribution tails to the left.

$$k = \frac{\Sigma\,(X_i - \overline{X})^3}{n\sigma^3}$$

*Standard Deviation* ($\sigma$), ($s$). The most widely used measure of dispersion of a set of data. It is equal to the square root of the variance and indicates the deviation of 68% of the values around the mean, and $1.96\sigma$, the deviation of 95% of the values around the mean. $\sigma$, the *standard deviation*, is the measure of the deviation of the universe. However, in most experimental work with limited sampling and in this study only an *estimated standard deviation* ($s$) is measurable. This differs in calculation in that $n$-1 rather than $n$ is used as the denominator. In this study and in further studies, $s$ and $s^2$ not $\sigma$ and $\sigma^2$ will be used to measure deviation of the data. They will be referred to as the *standard deviation* and *variance* respectively.

$$\sigma = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n}$$

$$s = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}$$

*t-test*. The difference in analyzed and true value expressed as ratio over the *standard deviation*. The value obtained is compared with critical values in a table. If the calculated t-value exceeds the theoretical t-value, the analyzed value is probably not from the same population as the rest of the data and can be rejected.

$$\text{t-value} = \frac{X_n - \text{true value}}{\textit{Standard Deviation } (s)}$$

*Variance* ($\sigma^2$), ($s^2$). The average of the squares of the deviations of a group of numbers from their average, $\bar{X}$.

$$\sigma^2 = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n}$$

$$s^2 = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}$$

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